Enargite Treatments and Pressure Oxidation of Concentrates

Kimberly Conner[1], Corby Anderson[*2]

Department of Metallurgical & Materials Engineering, Colorado School of Mines
1500 Illinois Street, Golden, Colorado, USA

[1]kconner@mines.edu; [*2]cganders@mines.edu

Abstract

Due to increasingly stringent worldwide environmental regulations for gaseous, aqueous and solid waste emissions, conventional smelting technology causes difficulties when treating materials containing arsenic. Many globally significant copper properties have copper sulfide mineralogy that has a high arsenic content present as enargite. Often, the enargite is present as very large resources with significant amounts of contained precious metals. As global copper, silver and gold demand increases while significant world resources decrease, treatment of sulfide orebodies with enargite is becoming increasingly important. A review of enargite treatment technologies are discussed as well as a basic overview of an evaluation of the selective dissolution and fixation of arsenic while leaving behind a clean copper and precious metals-bearing concentrate suitable as a smelter feed.

Keywords

Enargite; Pressure Oxidation; Arsenic

Introduction

When treated pyrometallurgically, arsenic minerals tend to decompose easily by forming oxides or sulfides that are volatile and report as a gas phase. Some stay in the metal phase and cause an impure final copper product.

High arsenic-containing concentrates can be smelted directly, but most copper smelters limit their total arsenic inputs for both environmental and economic reasons. The average arsenic level in custom copper concentrates has also been increasing, further limiting the potential market for high-arsenic enargite concentrates (Peacey, Gupta, and Ford 2010).

Properties of Enargite

Enargite, Cu_3AsS_4, is a blackish gray mineral with a metallic luster, Mohs hardness of 3, a density of 4.5 g/cm^3 and acts as a semiconductor. Copper is in the monovalent state, and arsenic in the pentavalent state. In most natural occurrances, enargite is associated with pyrite, and other copper and/or arsenic and/or base metal sulfides (chalcopyrite, chalcocite, covellite, digenite, tennantite, sphalerite, galena). Enargite may contain minor amounts of other elements (Sb, Ag, Fe). The presence of Sb (up to 6 wt %) is quite common, and important from an environmental point of view; enargite is frequently associated with Sb-bearing minerals (Lattanzi et al. 2008).

Enargite is a complex copper-arsenic sulfide mineral, that typically contains significant gold and silver values, and poses many process challenges. Large enargite deposits are found in Chile as well as other countries and the increasing demand for copper and gold have encouraged research into developing more effective methods of extracting metals of value from enargite concentrates (Peacey, Gupta, and Ford 2010).

The compound $Cu_3(As,Sb)S_4$ occurs naturally in two crystallographic forms: orthorhombic and tetragonal. The orthorhombic form is enargite (Cu_3AsS_4) and the tetragonal forms are luzonite (Cu_3AsS_4) and famatinite (Cu_3SbS_4) (Springer 1969). It has been suggested that enargite is a high temperature modification of luzonite (Maske and Skinner 1971).

Enargite Surface Properties

In a study of the surface properties of enargite as a function of pH, it was observed that the sign and magnitude of enargite's zeta potential is governed by the adsorption of the hydrolysis products of the As-Cu-S-H_2O system formed at the mineral/solution interface. The zeta potential of enargite was found to be quite sensitive to changes in pH, probably due to several simultaneous ionization and disassociation reactions (Castro and Baltierra 2005). Electrochemical oxidation and reduction of enargite were performed in 0.1 M HCl solution. The presence of Cu_{2+}, sulfate and chloride were detected at potentials above 0.2V, while at potentials below 0.6V the oxidation of arsenic was detected. Dissolved sulfur increased under reducing conditions forming H_2S and at oxidizing conditions forming sulfoxy species. The sulfur was believed to be

responsible for the observation of an active-passive transition at 0.3V (SCE) (Ásbjörnsson et al. 2004).

Selective flotation of synthetic enargite (18.94% As) from natural chalcopyrite under varied pulp potentials was conducted to investigate the feasibility of enargite removal from a chalcopyrite concentrate. The sample for flotation consisted of 50% synthetic enargite and 50% natural chalcopyrite. The test results indicate that chalcopyrite began to oxidize quickly at a much lower potential than enargite. Selective flotation revealed that enargite can be successfully removed from chalcopyrite through controlling the pulp potential above +0.2V and below +0.55V (SCE). The flotation results show that at a pulp potential of 0.5V (SCE), 93.4% enargite was floated into the concentrate with a grade of 92.8% enargite, and 92.6% chalcopyrite was recovered in the tailings at 93.2% chalcopyrite (Guo and Yen 2005). The electrochemical behavior of natural enargite in an alkaline solution was studied under conditions pertinent to those used in flotation of sulfide minerals. Photoelectrochemical experiments confirmed that the samples studied were p-type semiconductors. The potential range where the photocurrent was noticeable (below -0.4 ±0.2V vs. SCE) is more negative than the potential range of flotation (near 0.0V vs. SCE). It is believed that a surface layer forms over the potential range studied, and the law for the growth of this layer corresponds to two processes: the formation and dissolution of the layer (Pauporté and Schuhmann 1996).

The oxidation of synthetic and natural samples of enargite and tennantite were compared through dissolution and zeta potential studies. The changes in zeta potential with pH and oxidizing conditions are consistent with the presence of a copper hydroxide layer covering a metal-deficient sulfur-rich surface. The amount of copper hydroxide coverage increases with oxidation conditions. Arsenic dissolution was much lower than copper and does not appear to contribute to the mineral oxidation. The work showed that the natural samples of tennantite and enargite oxidize more than the synthetic samples in alkaline conditions, and tennantite oxidizes more than enargite (Fullston, Fornasiero, and Ralston 1999a). The surface oxidation of synthetic and natural samples of enargite and tennantite were monitored by X-ray photoelectron spectroscopy (XPS). The XPS results showed that the oxidation layer on the mineral surface is thin and the products are comprised of copper and arsenic oxide/hydroxide, sulfite, and a sulfur-rich layer of metal-deficient sulfide and/or polysulfide (Fullston,

Fornasiero, and Ralston 1999b). These two studies provided a qualitative perspective on the species present at the mineral surface.

Work was performed to investigate the effect of milling in different atmospheres on the leaching of enargite with HCl. Extended ball milling of enargite concentrate for 50 hours in an argon atmosphere resulted in little change in solubility. An air atmosphere showed a slow increase in dissolution with increased milling. The milling of enargite in an oxygen atmosphere at elevated temperature led to increased linear solubility of enargite due to the formation of $CuSO_4$ and As_2O_3, both of which are soluble in the 0.5M HCl leachant. The oxygen partial pressure, following first-order kinetics, appeared to have the largest effect. (Welham 2001).

Enargite Treatments

Pyrometallurgical Processing

Pyrometallurgical processing of enargite concentrates has been shown to remove arsenic, but the problem is handling of the arsenic-containing species and long term stability (Kusik and Nadkarni 1988). Decomposition of enargite in a nitrogen atmosphere at 575-700°C proceeded in two sequential steps forming tenantite as an intermediate compound (Padilla, Fan, and Wilkomirsky 2001). Sulfidation of chalcopyrite-enargite concentrate at 350-400°C resulted in rapid conversion of the chalcopyrite to covellite and pyrite. This was followed by pressure leaching in sulfuric acid with oxygen (Padilla, Vega, and Ruiz 2007).

One commercial process for treating large quantities of enargite concentrates is the Outotec Partial Roasting Process. It includes partial roasting at 600-750°C to produce a low-arsenic calcine and arsenic trioxide for sale or storage. The low-arsenic calcine was sold to copper smelters. The sale of significant amounts of arsenic trioxide is no longer possible but scrubbing from copper smelter gases and fixation in an environmentally acceptable manner is well-proven (Lattanzi et al. 2008; Peacey, Gupta, and Ford 2010).

The Namibia Custom Smelter (NCS), owned by Dundee Precious Metals, Inc. (DPM), is located in Tsumeb, Namibia which is approximately 430 km north of the capital, Windhoek. The smelter is one of only a few in the world able to treat arsenic and lead bearing copper concentrate. Chelopech, also owned by DPM, sends their concentrate to be processed by this smelter. For the year of 2011, NCS processed 88,514 mt of Chelopech concentrate and 91, 889 mt of

concentrate from third parties for a total of 180,403 mt. Since acquiring NCS in 2010, DPM embarked on an expansion and modernization program designed to bring the smelter into the 21st century from a health, safety and environmental perspective. The first phase of the project was designed to address arsenic handling. They expanded the Ausmelt furnace, a superior furnace from an environmental point of view, enabling them to perform all primary smelting through the Ausmelt, allowing the older reverbatory furnace to be used as a holding furnace. A new baghouse was also being installed and all the existing systems designed to manage the arsenic were upgraded. Upon completion of the two phases of the project, the specialty smelter at Tsumeb will be repositioned to be one of the most unique smelters in the world, with the ability to treat DPM and third party complex concentrates in a responsible and sustainable manner that meets Namibian as well as global health, safety and environmental standards ("Annual Review 2011" 2012).

Hydrometallurgical Processing

Several new hydrometallurgical processes have been developed to treat copper sulfide concentrates and may be suitable for enargite including atmospheric leaching, bio-oxidation and pressure oxidation. The advantage of hydrometallurgy over roasting is that the arsenic can be precipitated directly within the leach reactor as ferric arsenate (Peacey, Gupta, and Ford 2010).

The study of the separation of enargite and tennantite from non-arsenic copper sulfide minerals by selective oxidation or dissolution showed that it is difficult to use flotation to separate chalcocite, covellite or chalcopyrite from enargite or tennantite under normal oxidation conditions. Improved separation occurred at pH 5.0 after selective oxidation with H_2O_2, or at pH 11.0 after oxidation with H_2O_2 followed by EDTA addition to selectively remove surface oxidation products (Fornasiero et al. 2001).

Bulk oxidation of enargite in air is a slow process. Thermodynamics suggests that enargite should not be stable in acidic solutions. At acidic to neutral pH, oxidation/dissolution is slow but is accelerated by the presence of ferric iron and/or bacteria (Lattanzi et al. 2008).

Arsenic dissolved from concentrate by leaching enargite with sodium hypochlorite under alkaline oxidizing conditions where the enargite is converted into crystalline CuO and arsenic dissolves forming AsO_4^{3-}. The reaction rate was very fast and chemically controlled (Curreli et al. 2005; Vinals et al. 2003).

Dissolution of enargite in acidified ferric sulfate solutions at 60-95°C yielded elemental sulphur, sulfate sulfur and sulfate with dissolved copper and arsenic. The dissolution kinetics were linear and copper extraction increased with increasing ferric sulfate and sulfuric acid concentration (Dutrizac and MacDonald 1972). Leaching of enargite in acidic sulfate and chloride media resulted in complete dissolution at temperatures above 170°C (Riveros, Dutrizac, and Spencer 2001). At <100°C, enargite dissolves slowly in either $Fe(SO_4)_{1.5}$ or $FeCl_3$ media, and the dissolution rate obeys the shrinking core model. The rate increases with increasing temperature and the apparent activation energies are 50-64 kJ/mol. The rate increases slightly with increasing $FeCl_3$ concentrations in 0.3M HCl media. The leaching of enargite at elevated temperatures and pressures was also investigated. Potentially useful leaching rates are achieved above 170°C, at which temperature sulfate, rather than sulfur, is produced. Lower temperatures (130-160°C) lead to fast initial leaching rates, but the dissolution of the enargite is incomplete because of the coating of the enargite particles by elemental sulfur (Riveros and Dutrizac 2008).

Enargite dissolution in ammoniacal solutions was slow and 60% of copper was extracted after 14 hours (Gajam and Raghavan 1983).

In the case of gold-bearing enargite concentrates, leaching with basic Na_2S has been shown to selectively solubilize the arsenic, and some gold, but does not affect the copper. The copper is transformed in the leach residue to a species $Cu_{1.5}S$ and the gold is partly solubilized in the form of various anionic Au-S complexes. The gold and arsenic could then be recovered from solution. The author did not quantify the gold leached (Curreli et al. 2009). Other work had indicated that leaching with sodium sulfide in 0.25M NaOH at 80-105°C will dissolve sulfides of arsenic, antimony and mercury (Nadkarni and Kusik 1988; C. G. Anderson 2005; C. Anderson and Twidwell 2008). The selective leaching of antimony and arsenic from mechanically activated tetrahedrite, jamesonite and enargite in alkaline solution of sodium sulfide is temperature-sensitive. (Baláz and Achimovicová 2006). The treatment of copper ores and concentrates with industrial nitrogen species catalyzed pressure leaching and non-cyanide precious metals recovery was

effective in leaching copper and oxidizing the sulfide to sulfate in a minimum amount of time while keeping the arsenic out of solution through in-situ precipitation (C. G. Anderson 2003).

Bornite, covellite and pyrite were reacted hydrothermally with copper sulfate solutions at pH 1.1-1.4 to produce digenite which was then transformed to djurleite, chalcocite, and chalcocite-Q and trace djurleite respectively. The bornite reaction is diffusion controlled while the covellite and pyrite are chemically controlled. A Chilean copper concentrate was hydrothermally treated at 225-240°C with copper sulfate solutions to remove impurities. The mineral phases behaved in a similar manner as described above. Arsenic was described as being moderately eliminated (20-40%) (Fuentes, Vinals, and Herreros 2009a; Fuentes, Vinals, and Herreros 2009b). Hydrothermally reacting sphalerite with acidified copper sulfate solution by metathesis reaction at 160-225°C resulted in digenite at lower temperature and chalcocite at higher temperature. Copper sulfide formed in a compact layer around a core of sphalerite retaining the same size and shape of the original particle. The work shows that sphalerite could be removed from a digenite or chalcopyrite copper concentrate (Vinals, Fuentes, Hernandez and Herreros 2004).

Complete dissolution of enargite at 220°C, 100 psi in 120 minutes was achieved and found a sulfuric acid content over 0.2 molar had a negligible effect on dissolution (Padilla, Rivas, and Ruiz 2008). Leaching of enargite in sulfuric acid, sodium chloride, and oxygen media found arsenic dissolution was very slow. About 6% of the arsenic dissolved in 7 hours at 100°C (Padilla, Giron, and Ruiz 2005). Enargite dissolved faster when pressure leaching in the presence of pyrite at 160-200°C than the dissolution of pure enargite which is thought to be the result of ferric ions (Ruiz, Vera, and Padilla 2011).

Bio-Oxidation

Enargite was leached faster by bacteria in sulfuric acid with ferric sulfate than by chemical leaching at the same or higher ion concentration (Escobar, Huenupi, and Wiertz 1997). Arsenic-bearing copper ores and concentrates could be leached by Sulfolobus BC in the presence of ferric iron due to precipitation of ferric arsenate (Escobar et al. 2000). In evaluating bio-oxidation of a gold concentrate prior to cyanidation of high pyrite and enargite content, the bacterial attack was directed toward pyrite with minimal effect on the enargite (Canales, Acevedo, and Gentina 2002). The electrochemical study of enargite bioleaching by mesophilic and thermophilic microorganisms showed that enargite dissolution increased at higher temperatures, or thermophilic conditions (Munoz et al. 2006). Leach tests on composited sulfide ores containng enargite and covellite achieved higher copper extraction at thermophilic conditions than mesophilic conditions (Lee et al. 2011). Arsenic-tolerant acidithiobacillus ferrooxidans achieved oxidation dissolution of enargite by forming elemental sulfur, arsenate and oxidized sulfur species (Sasaki et al. 2009). The study of CO_2 supply on the biooxidation of an enargite-pyrite gold concentrate showed a marked effect on the kinetics of growth and bioleaching. Four percent carbon dioxide resulted in the best suspended cell population as well as maximum extraction of Fe, Cu and As (Acevedo, Gentina, and García 1998).

Other Processing Technologies

A pyro-hydrometallurgical approach is the acid-bake leach which achieved approximately 90% copper extraction when baking at 200°C with less than 1% of arsenic reporting to the gas phase. Results show that upon baking with 5 grams concentrated sulfuric acid per gram of contained copper, the enargite, chalcopyrite, sphalerite and galena will be converted to their corresponding sulfates (Safarzadeh, Moats, and Miller 2012a; Safarzadeh, Moats, and Miller 2012b).

Arsenic Fixation

Because arsenic is most hazardous when mobile, it must be fixed to get it in a stable form for long-term storage. Two stable forms include ferrihydrite and scorodite.

In treating hydrometallurgical solutions and waste streams for the removal of arsenic, the use of coprecipitation with Fe(III) has been specified by the US EPA as the Best Demonstrated Available Technology (BDAT). This technology has been widely adopted over the last century, and developments have been well reviewed (L. G. Twidwell, Robins, and Hohn 2005). This technology has also been selected as one of the Best Available Technologies (BAT) for removing arsenic from drinking waters (L. Twidwell and McCloskey 2011).

Two ferric precipitation arsenic removal technologies are presently practiced by industry: ambient temperature ferrihydrite/arsenic co-precipitation and elevated temperature precipitation of ferric arsenate.

The ambient temperature technology is relatively simple and the presence of commonly associated metals such as copper, lead and zinc and gypsum have a stabilizing effect on the long term stability of the product. The disadvantages of the adsorption technology are the formation of voluminous waste material that is difficult to filter, the requirement that the arsenic be present in the fully oxidized state as arsenate, and the question as to long term stability of the product in the presence of reducing substances. The disadvantages of the ferric arsenate precipitation are that the treatment process is more capital intensive, the compound may dissolve incongruently if the pH is >4, and it may not be stable under reducing or anaerobic bacterial conditions (L. G. Twidwell, Robins, and Hohn 2005).

The production of scorodite, especially from arsenic-rich and iron-deficient sulfate solutions offers a number of operational advantages such as high arsenic content, stoichiometric iron demand, and excellent dewatering characteristics.

There are two process options of industrial relevance; the hydrothermal option that involves autoclave processing at elevated temperature (≥150°C) and pressure and the atmospheric process based on supersaturation-controlled precipitation of scorodite at 90-95°C.

In addition to hydrothermal production of scorodite the work done by Demopoulos has determined that it is feasible to produce scorodite by step-wise lime neutralization at 90°C. The atmospheric scorodite possesses the same structural and solubility characteristics with the hydrothermally produced scorodite. Thermodynamic calculations determined that scorodite is stable in the presence of ferrihydrite under oxic conditions up to pH 6.75 at 22°C or higher pH at lower temperature and gypsum-saturated solutions (Demopoulos 2005).

Pressure Oxidation

Many companies have been investigating hydrometallurgical treatment methods for the leaching of copper concentrates as an alternative to conventional smelting technology by pressure oxidation. Freeport-McMoRan Copper&Gold has developed a sulfate-based pressure leaching technology for the treatment of copper sulfide concentrates. The main drivers for the activity were the relatively high and variable cost of external smelting and refining capacity, the limited availability of smelting and refining capacity and the need to cost-effectively generate sulfuric acid at mine sites for use in stockpile leaching operations. Freeport-McMoRan Copper & Gold or FCX was looking to treat chalcopyrite concentrates with this technology and developed both high and medium temperature processes (Marsden, Wilmot, and Hazen 2007a); (Marsden, Wilmot, and Hazen 2007b).

Anaconda Copper Company performed work on ores from the Butte area to evaluate the possibility of converting chalcopyrite to digenite at about 200°C to upgrade and clean the concentrate to the point where it could be shipped as a feed to a copper smelter. They showed that this reaction is possible and a significant amount of the iron and arsenic (along with other impurities) were removed from the solid product while retaining the majority of the copper, gold and silver in the concentrate. The upgrading process also results in a lower mass of concentrate to ship, thereby decreasing shipping costs. Primarily, the process consists of chemical enrichment that releases iron and sulfur from the chalcopyrite, followed by solid-liquid separation with treatment of the liquid effluent. This is followed by flotation with recycle of the middling product back to the enrichment process and rejection of the tailing. The resultant product is digenite formed as a reaction product layer around the shrinking core of each chalcopyrite grain. About 80% of the zinc impurities reported to the liquor, while arsenic, bismuth and antimony were evenly distributed between the discharge liquor and the enriched product. Gold, silver and selenium followed the copper (Bartlett 1992); (Bartlett et al. 1986).

Research Approach

The work at Colorado School of Mines was performed on a copper-enargite concentrate sample. The investigation was devoted to the specific objectives below:

1. A detailed thermodynamic evaluation of the effects of pressure, temperature and redox potential on the fate of the minerals present in the enargite. The evaluation includes the reactions taking place during the oxidation process, the corresponding values of enthalpy of reaction and equilibrium constants, and prediction of phase stability with varying conditions.

2. The use of a laboratory batch autoclave to perform the experiments.

3. Developing an understanding of the kinetics of the proposed reactions, the products that are formed and the fate of the deleterious impurity elements.

4. Mineralogical characterization of the feed materials and leached solid products to optimize and confirm the desired copper phase transformation.

5. Design-of-Experimentation-based testing and modeling to quantify effects and interactions based on experimental factors.

6. Fixation of arsenic from solution as ferrihydrite or scorodite.

Eh-pH diagrams were generated using Stabcal for enargite illustrating other solid copper phases are shown below:
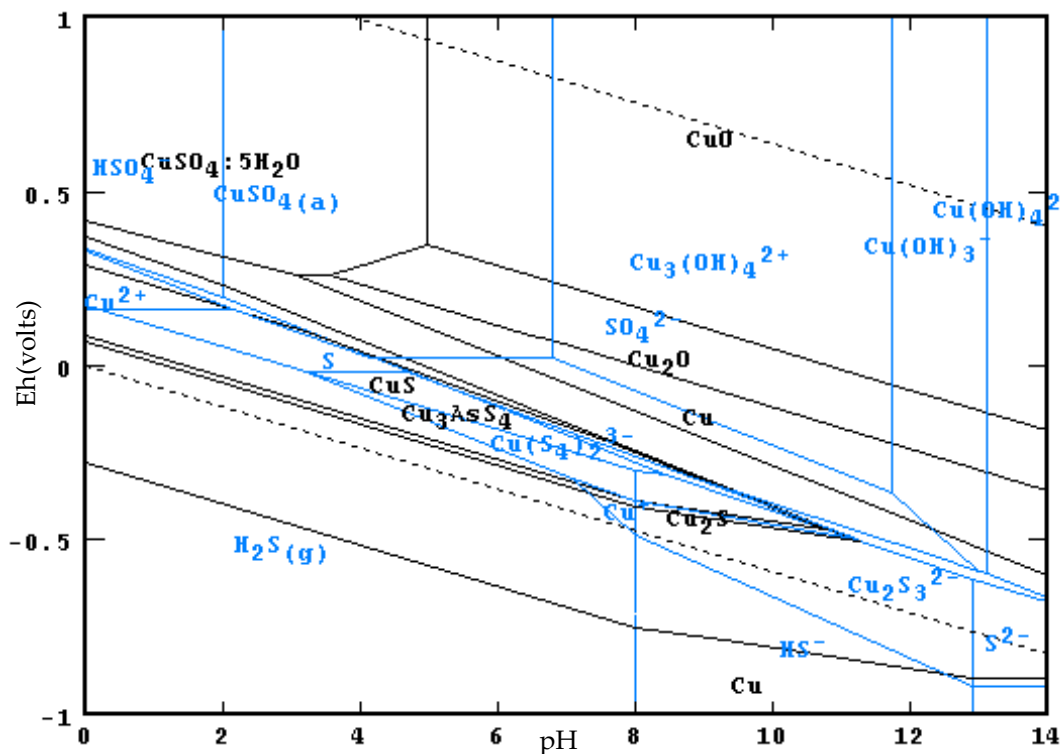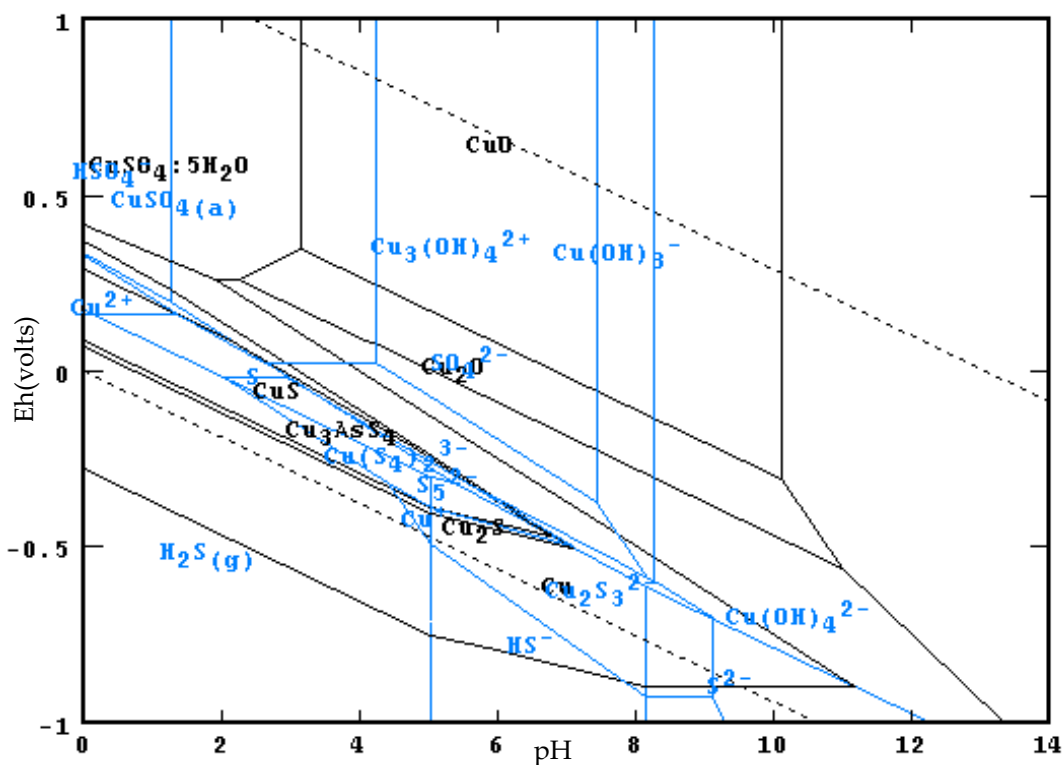
FIG. 1 Eh-pH DIAGRAM AT 25°C

FIG. 2 Eh-pH DIAGRAM AT 200°C

The experimental work is subject to confidentiality constraints agreed to with Freeport-McMoRan Copper and Gold.

REFERENCES

Acevedo, F., J. C. Gentina, and N. García. 1998. "CO$_2$ Supply in the Biooxidation of an Enargite-pyrite Gold Concentrate." Biotechnology Letters 20 (3): 257–259.

Anderson, C. G. 2003. "Treatment of Copper Ores and Concentrates with Industrial Nitrogen Species Catalyzed Pressure Leaching and Non-cyanide Precious Metals Recovery." JOM Journal of the Minerals, Metals and Materials Society 55 (4): 32–36.

Anderson, C.G. 2005. "The Treatment of Arsenic Bearing Ores, Concentrates and Materials with Alkaline Sulfide Hydrometallurgy." In Arsenic Metallurgy, 255–263. San Francisco, CA: TMS.

Anderson, CG, and LG Twidwell. 2008. "Hydrometallurgical Processing of Gold-Bearing Copper Enargite Concentrates." Canadian Metallurgical Quarterly 47 (3): 337–346.

"Annual Review 2011." 2012. Dundee Precious Metals, Inc.

Ásbjörnsson, J., G. H. Kelsall, R. A. D. Pattrick, D. J. Vaughan, P. L. Wincott, and G. A Hope. 2004. "Electrochemical and Surface Analytical Studies of Enargite in Acid Solution." Journal of the Electrochemical Society 151: E250–E256.

Baláz, P., and M. Achimovicová. 2006. "Selective Leaching of Antimony and Arsenic from Mechanically Activated Tetrahedrite, Jamesonite and Enargite." International Journal of Mineral Processing 81 (1): 44–50.

Bartlett, R. W. 1992. "Upgrading Copper Concentrate by Hydrothermally Converting Chalcopyrite to Digenite." Metallurgical and Materials Transactions B 23 (3): 241–248.

Bartlett, R. W., D. B. Willson, B. J. Savage, and R. J. Wesely. 1986. "A Process For Enriching Chalcopyrite Concentrates." Hydrometallurgical Reactor Design and Kinetics: 227–246.

Canales, C., F. Acevedo, and J. C Gentina. 2002. "Laboratory-scale Continuous Bio-oxidation of a Gold Concentrate of High Pyrite and Enargite Content." Process Biochemistry 37 (10): 1051–1055.

Castro, S. H., and L. Baltierra. 2005. "Study of the Surface Properties of Enargite as a Function of pH." International Journal of Mineral Processing 77 (2): 104–115.

Curreli, L., C. Garbarino, M. Ghiani, and G. Orrų. 2009. "Arsenic Leaching from a Gold Bearing Enargite Flotation Concentrate." Hydrometallurgy 96 (3): 258–263.

Curreli, L., M. Ghiani, M. Surracco, and G. Orrų. 2005. "Beneficiation of a Gold Bearing Enargite Ore by Flotation and As Leaching with Na-hypochlorite." Minerals Engineering 18 (8): 849–854.

Demopoulos, G.P. 2005. "On the Preparation and Stability of Scorodite." In Arsenic Metallurgy, 25–50. San Francisco, CA: TMS.

Dutrizac, J. E., and R. J. C. MacDonald. 1972. "The Kinetics of Dissolution of Enargite in Acidified Ferric Sulphate Solutions." Canadian Metallurgical Quarterly 11 (3): 469–476.

Escobar, B., E. Huenupi, I. Godoy, and J. V Wiertz. 2000. "Arsenic Precipitation in the Bioleaching of Enargite by Sulfolobus BC at 70° C." Biotechnology Letters 22 (3): 205–209.

Escobar, B., E. Huenupi, and J. V Wiertz. 1997. "Chemical and Biological Leaching of Enargite." Biotechnology Letters 19 (8): 719–722.

Fornasiero, D., D. Fullston, C. Li, and J. Ralston. 2001. "Separation of Enargite and Tennantite from Non-arsenic Copper Sulfide Minerals by Selective Oxidation or Dissolution." International Journal of Mineral Processing 61 (2): 109–119.

Fuentes, G., J. Vinals, and O. Herreros. 2009a. "Hydrothermal Purification and Enrichment of Chilean Copper Concentrates:: Part 1: The Behavior of Bornite, Covellite and Pyrite." Hydrometallurgy 95 (1-2): 104–112.

———. 2009b. "Hydrothermal Purification and Enrichment of Chilean Copper Concentrates. Part 2: The Behavior of the Bulk Concentrates." Hydrometallurgy 95 (1-2): 113–120.

Fullston, D., D. Fornasiero, and J. Ralston. 1999a. "Oxidation of Synthetic and Natural Samples of Enargite and Tennantite: 1. Dissolution and Zeta Potential Study."

Langmuir 15 (13): 4524–4529.

———. 1999b. "Oxidation of Synthetic and Natural Samples of Enargite and Tennantite: 2. X-ray Photoelectron Spectroscopic Study." Langmuir 15 (13): 4530–4536.

Gajam, S., and S. Raghavan. 1983. "A Kinetic Study of Enargite Dissolution in Ammoniacal Solutions." International Journal of Mineral Processing 10 (2): 113–129.

Guo, H., and W.-T. Yen. 2005. "Selective Flotation of Enargite from Chalcopyrite by Electrochemical Control." Minerals Engineering 18 (6): 605–612.

Kusik, C.L., and R.M. Nadkarni. 1988. "Pyrometallurgical Removal of Arsenic from Copper Concentrates." In Arsenic Metallurgy Fundamentals and Applications, 263–286. Phoenix, AZ: TMS.

Lattanzi, P., S. Da Pelo, E. Musu, D. Atzei, B. Elsener, M. Fantauzzi, and A. Rossi. 2008. "Enargite Oxidation: A Review." Earth-Science Reviews 86 (1-4): 62–88.

Lee, J., S. Acar, D. L Doerr, and J. A Brierley. 2011. "Comparative Bioleaching and Mineralogy of Composited Sulfide Ores Containing Enargite, Covellite and Chalcocite by Mesophilic and Thermophilic Microorganisms." Hydrometallurgy 105 (3): 213–221.

Marsden, J. O., J. C. Wilmot, and N. Hazen. 2007a. "Medium-temperature Pressure Leaching of Copper concentrates-Part I-Chemistry and Initial Process Development." Minerals and Metallurgical Processing 24 (4): 193–204.

———. 2007b. "Medium-temperature Pressure Leaching of Copper concentrates-Part II-Development of Direct Electrowinning and an Acid-autogenous Process." Minerals and Metallurgical Processing 24 (4): 205–217.

Maske, Siegfried, and Brian J. Skinner. 1971. "Studies of the Sulfosalts of Copper; I, Phases and Phase Relations in the System Cu-As-S." Economic Geology 66 (6): 901–918.

Munoz, J. A., M. L. Blazquez, F. Gonzalez, A. Ballester, F. Acevedo, J. C. Gentina, and P. Gonzalez. 2006. "Electrochemical Study of Enargite Bioleaching by Mesophilic and Thermophilic Microorganisms." Hydrometallurgy 84 (3-4): 175–186.

Nadkarni, R.M., and C.L. Kusik. 1988. "Hydrometallurgical Removal of Arsenic from Copper Concentrates." In Arsenic Metallurgy Fundamentals and Applications, 263–286. Phoenix, AZ: TMS.

Padilla, R., Y. Fan, and I. Wilkomirsky. 2001. "Decomposition of Enargite in Nitrogen Atmosphere." Canadian Metallurgical Quarterly 40 (3) (January 1): 335–342.

Padilla, R., D. Giron, and M. C. Ruiz. 2005. "Leaching of Enargite in H2SO4-NaCl-O2 Media." Hydrometallurgy 80 (4): 272–279.

Padilla, R., C. A. Rivas, and M. C. Ruiz. 2008. "Kinetics of Pressure Dissolution of Enargite in Sulfate-Oxygen Media." Metallurgical and Materials Transactions B 39 (3): 399–407.

Padilla, R., D. Vega, and M. C Ruiz. 2007. "Pressure Leaching of Sulfidized Chalcopyrite in Sulfuric Acid-oxygen Media." Hydrometallurgy 86 (1-2): 80–88.

Pauporté, T., and D. Schuhmann. 1996. "An Electrochemical Study of Natural Enargite Under Conditions Relating to Those Used in Flotation of Sulphide Minerals." Colloids and Surfaces A: Physicochemical and Engineering Aspects 111 (1-2): 1–19.

Peacey, John G., Mark Z. Gupta, and Kevan J.R. Ford. 2010. "Review of Process Options to Treat Enargite Concentrates." In Proceedings of Copper 2010, 3:1035–1050. Hamburg, Germany: GDMB.

Riveros, P. A., and J. E. Dutrizac. 2008. "The Leaching of Tennantite, Tetrahedrite and Enargite in Acidic Sulphate and Chloride Media." Canadian Metallurgical Quarterly 47 (3): 235–244.

Riveros, P. A., J. E. Dutrizac, and P. Spencer. 2001. "Arsenic Disposal Practices in the Metallurgical Industry." Canadian Metallurgical Quarterly 40 (4): 395–420.

Ruiz, M.C., M.V. Vera, and R. Padilla. 2011. "Mechanism of Enargite Pressure Leaching in the Presence of Pyrite." Hydrometallurgy 105 (3-4) (January): 290–295. doi:16/j.hydromet.2010.11.002.

Safarzadeh, M. Sadegh, Michael S. Moats, and Jan D. Miller. 2012a. "Acid Bake-leach Process for the Treatment of Enargite Concentrates." Hydrometallurgy. http://www.sciencedirect.com/science/article/pii/S0304386X12000606.

———. 2012b. "Recent Trends in the Processing of Enargite Concentrates." Mineral Processing and Extractive Metallurgy Review (just-accepted). http://www.tandfonline.com/doi/abs/10.1080/08827508.2012.723651.

Sasaki, K., K. Takatsugi, T. Hirajima, N. Kozai, T. Ohnuki,

and O. H Tuovinen. 2009. "Bioleaching of Enargite by Arsenic-Tolerant Acidithiobacillus Ferrooxidans." Advanced Materials Research 71: 485–488.

Springer, G. 1969. "Compositional Variations in Enargite and Luzonite." Mineralium Deposita 4 (1): 72–74.

Twidwell, L.G., R.G. Robins, and J.W. Hohn. 2005. "The Removal of Arsenic from Aqueous Solution by Coprecipitation with Iron (III)." In Arsenic Metallurgy, 3–24. San Francisco, CA: TMS.

Twidwell, LG, and JW McCloskey. 2011. "Removing Arsenic from Aqueous Solution and Long-term Product Storage." JOM Journal of the Minerals, Metals and Materials Society 63 (8): 94–100.

Vinals, J., A. Roca, M. C. Hernandez, and O. Benavente. 2003. "Topochemical Transformation of Enargite into Copper Oxide by Hypochlorite Leaching." Hydrometallurgy 68 (1-3): 183–193.

Welham, N. J. 2001. "Mechanochemical Processing of Enargite (Cu3AsS4)." Hydrometallurgy 62 (3): 165–173.

Kimberly D. Conner earned a Bachelor of Science degree in metallurgical and materials engineering from the Colorado School of Mines in Golden, Colorado in 2006 and is currently pursuing a Doctor of Philosophy in metallurgical and materials engineering from Colorado School of Mines to be completed in fall 2013.

She has worked as a Metallurgical Engineer for Newmont Gold Corporation at the Malozemoff Technical Facility in Englewood, Colorado since May 2013. She has worked as a Research Engineer for Freeport-McMoRan Copper and Gold at their Process Technology Center in Safford, Arizona from 2006-2008. She worked as a Draftsman/Intern for Reynolds Engineering Company in Alamosa, Colorado from May to August 2003.

Ms. Conner is a professional member of SME and TMS and has served on the SME MPD Separations Unit Committee for 5 years, Student Member Affairs Committee for 3 years, and chaired several technical sessions at various SME Annual Meetings.

Corby G. Anderson holds a Bachelor of Science in Chemical Engineering, a Master of Science in Metallurgical Engineering and a PhD in Mining Engineering – Metallurgy. He has over 34 years of global experience in minerals, metals and chemicals. He has held positions of responsibility in industrial operations, management, research, consulting, design, teaching and professional sevice. He is a registered engineer and a member in good standing of multiple professional societies. Currently, he is the Harrison Western Professor of Metallurgical and Materials Engineering at the Colorado School of Mines in Golden Colorado.